The Second International Conference of Sciences and Engineering (ICES2024)
University of Sirte-Libya
26-27/5/2024

Examine the Adsorption of the New Polyester Derivative (GLYPTAL) Inhibitor on the Surface of Mild Steel

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ABSTRACT

A prior study that examined the effects of eco-friendly polyester (GLYPTAL) as an inhibitor on the corrosion behaviour of mild steel in 1 M hydrochloric corrosive acid solutions used the weight loss technique at room temperature. The inhibitory impact was considered by altering the inhibitor concentrations (100, 200, 400, 500, and 1000 ppm by weight of the solution). Mild steel corrosion was consistently stifled with the amount of inhibitor used. It obtained a high state of inhibition at inhibitor concentrations of 500 and 1000 ppm. In the current work, the adsorption of a (GLYPTAL) inhibitor on the surface of mild steel was examined. A variety of adsorption isotherms, including Langmuir, Temkin, Freundlich, Adejo Ekwenchi, and El-Awady, were used in the adsorption experiment. The (GLYPTAL) inhibitor complies with all used isotherm models, with Temkin isotherm having the best compliance (correlation factor $R^2 = 0.9964$), indicating that the inhibitor has extremely good adsorption on mild steel surfaces. On the other hand, a thermodynamics parameter (adsorption free energy, ($\Delta G°_{ads}$), based on their values, has been hypothesised as the adsorption mechanism, and the high value and negative sign show that the inhibitor's adoption on the metal surface was appropriate. To prepare your paper please use directly this template and simply replace this text by your text.

Keywords: *Mild Steel, Hydrochloric Acid Corrosion, Eco-Friendly Polyester Adsorption Isotherm Models, Inhibitor Surface coverage*

1. Introduction

Referring to the study conducted by Seham Shahen in 2019 [1], who evaluated the effect of eco-friendly Polyester (GLYPTAL) as an inhibitor on the corrosion behaviour of mild steel in hydrochloric acid (HCL) solution. It was found that these mild steel specimens in the presence of an inhibitor revealed that as the concentration

of the inhibitor increased, so did the rate of weight loss and corrosion. When the concentration of the inhibitor was 1000 ppm, which was its maximum weight, and the minimum corrosion rate was 1.41 $mg.cm^{-2}.hr^{-1}$, the maximum efficiency was discovered to be 90.72 %. The goal of the inhibitor is to bind either at the cathodic phase or the anionic part of the corrosion process because corrosion can be either cathodic or anionic. This reduces, if not entirely prevents, the metal's electrons or protons from reacting with the environment, such as water [2]. Inhibitors are frequently adsorbed to the metal's surface via chemical or physical adsorption to prevent or slow down corrosion. The ability of an inhibitor to bind to the surface of a metal determines how well it inhibits corrosion [2]. The link between the inhibitor and the solution as the mechanism of inhibiting corrosion can be shown using the equation below: $[Inhibitor]_{sol.} + [nH_2O]_{adsorbed} \sim [Inhibitor]_{adsorbed} + [nH_2O]_{sol.}$ [2]. Based on these factors, corrosion inhibition is a particular case of an electrochemical process being inhibited. Due to this, numerous researchers have examined the mechanisms underlying the effects of inhibitors, notably the organic inhibitors that are the subject of this work, using comparative assessments of corrosion inhibition [3, 4]. It is generally agreed that the inhibiting effect of organic compounds on the dissolution of metallic materials is caused by interactions by adsorption between the inhibitor and the metal surface, despite the fact that some authors think this phenomenon only represents the initial stage of the actual inhibition process [3]. The sort of interaction involved can be determined by examining the adsorption kinetics, the heat of adsorption, or the reversibility and specificity of the bond formed [3].

Physically adsorbed species interact fast with the electrode due to electrostatic or van der Waals forces, but they can be easily removed from the surface, for example by dipping the metal into an inhibitor-free solution. During the chemisorption process, charge sharing or charge transfer happens more slowly and with more adsorption heat. Only a few metals are affected by this adsorption, and it is only partially reversible [3, 5].

Comparing the aforementioned qualities reveals that chemisorptions, which can range from straightforward adsorption to the construction of actual physical barriers, are often necessary for an efficient inhibitory action. Numerous authors have proposed various general Many authors have put forth a variety of general theories for how inhibitors function, such as an increase in the proton discharge process's overvoltage, which forms the partial cathodic reaction of the corrosion process, an increase in ohmic resistance because an inhibitor film is present at the metal-solution interface, or nonspecific adsorption phenomena. [3 - 6]. Through an examination of

the relationships between molecular structure and inhibitor properties, these hypotheses have been supplemented and given better definition. A thorough analysis of the electrochemical behaviour of metallic materials in the presence of inhibitors, an in-depth evaluation of the potential dependence of the adsorption phenomena, and a better comprehension of the energy parameters involved in the interaction between inhibitors and metallic materials have all significantly improved our understanding of the phenomenon [3]. The manuscript title must be in "Title Case", i.e., when writing a name or a title, you should only use capital letters for the principal words. Do not use capital letters for prepositions, articles or conjunctions unless one is the first word.

2. Measurements and Units Results of Corrosion Rate and Inhibitor Efficiency Related to Reference [1].

Table (1) displays the results of corrosion tests performed on carbon steel specimens in desalination water, in accordance with the study in Ref. [1]. These results have been utilized to analyses the adsorption of inhibitor on the carbon steel surface using a number of adsorption isotherm models.

Table (1) Corrosion Rate and Inhibitor Efficiency Related to Ref. [1].

Sample No.	**1**	**2**	**3**	**4**	**5**	**6**
Inhibitor (Concentration) (ppm)	Blank	100	200	400	500	1000
Corrosion Rate ($mg.cm^{-2}.hr^{-1}$)	15.28	04.99	04.15	02.92	02.62	01.41
Efficiency of Inhibitor (IE) (%)	-	67.32	72.79	80.86	82.85	90.72

3. Thermodynamic Parameters of Adsorption of Eco-Friendly Polyester Aqueous HCL Medium

Thermodynamic parameters play an important role in understanding the inhibitive mechanism. The free energy of adsorption ($\Delta G°_{ads}$), which can characterize the interaction of adsorbed molecules and metal surface, was calculated using the equation:

$$(\Delta G°_{ads}) = - RT\ln (55.5 \times K_{ads}) \quad (1)$$

Where, K_{ads} is the adsorption equilibrium constant, R is the gas constant (8.314 J. $K^{-1}.mol^{-1}$), T is the absolute temperature in Kelvin and the value of 55.5 is the concentration of water in solution expressed in mol. L^{-1} [7]. The free energy of adsorption is related to the equilibrium constant K_{ads} of adsorption, which can be

calculated using the equation:

$$K_{ads} = \frac{\frac{\theta}{1-\theta}}{I_{inh}} \quad (2)$$

Thermodynamic parameter for adsorption of the Eco-Friendly Polyester (GLYPTAL) in aqueous HCL medium is given in Table (2). The stability of the absorbed layer on the electrode surface is ensured by the negative value of ($\Delta G°_{ads}$). In general, the values of ($\Delta G°_{ads}$) up to -20 KJ.mol^{-1} are constant with the electrostatic interaction between the charged molecules and charged metal (physisorption), whereas the negative values higher than - 40 KJ.mol^{-1} involve sharing or transfer of electrons from the inhibitors to the metal surface to form a co-ordinate type of bond [8].

Based on the experimental data presented in Table (2), the calculated value of ($\Delta G°_{ads}$) was found to be negative and less than 40 KJ.mol^{-1}. The values of ($\Delta G°_{ads}$) for (GLYPTAL) extract are in the ranges from -15.18 KJ.mol^{-1} to - 13.31 KJ.mol^{-1}, indicating that phyto-constituents are adsorbed on the metal surface by a strong physical adsorption process. The (GLYPTAL) components' strong and spontaneous adsorption on the metal surface is shown by the relatively large and negative free energy value, which accounts for its high corrosion index. Thus, physical adsorption is most likely the basis of the hypothesised mechanism for the (GLYPTAL) inhibitor system. In general, the inclusion of hetero atoms in the inhibitor molecules, such as N/O/S atoms with a lone pair of electrons, might boost the adsorption by causing the inhibitor molecules to become electrostatically adsorbed on the metal surface, generating insoluble stable coatings and reducing metal dissolution.

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4. Adsorption Isotherm Models

4.1 Introduction

It is well known that the inhibitors' adsorption is reliant on their structural makeup, and it is assumed this adsorption is closely related to the electrochemical reaction taking place on the metal surface [8, 10]. The adsorption of the inhibitor molecules from aqueous solution can be regarded as quasi-substitution process between organic compound in the aqueous phase Org_{aq} and water molecules at the electrode surface $(H_2O)_{sol}$, $Org_{sol} + x(H_2O)_{aq} = Org_{aq} + (H_2O)_{sol}$. Where, x (size ratio) is the number of water molecules in the inhibitor] [10].

The experimental results can be used to estimate the interaction of the surface

inhibitor. The kind, quantity of active sites on the metal surface, charge density, molecule size, interactions between the metal and the inhibitor, and creation of metallic complexes all affect how effective the inhibition is. Adsorption isotherms give information on the size, interactions between the metal and the inhibitor, and creation of metallic complexes all affect how effective the inhibition is. Adsorption isotherms give information on the metal inhibitor interactions [10].

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions, the most frequently used are those of Lungmir, Temkin, Frumkin, Frendlich, Adejo Ekwenchi and El-Awady. All these isotherms are of the general form:

$$f(\theta, x)\exp(-2a\theta) = K_{ads}.I_{inh} \quad (3)$$

Where, $f(\theta, x)$ is the configuration factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm, θ is the degree of the surface coverage, I_{inh} is the inhibitor concentration in the electrolyte, x is the size ratio indicating the number of water molecules displaced by one molecule of organic inhibitor, (a) is the molecular interaction parameter and (K_{ads}) is the equilibrium constant for the adsorption. In general, it is thought that the formation and maintenance of a protective film on the metal surface is what prevents corrosion [8]. It was assumed, in order to determine the surface coverage, that the inhibitor efficiency is mostly caused by the blocking effect of the adsorbed species and hence $K_{ads}.I_{inh}$ $\eta\% = (100)(\theta)$ [10]. The surface coverage data were theoretically fitted into various adsorption isotherms to obtain insight into the manner of the inhibitor's adsorption on the surface of carbon steel, and the values of the correlation coefficient (R^2) were utilised to select the isotherm that provided the best match [10].

4.2. Langmuir Adsorption Isotherm

The adsorptive capacity of various adsorbents is measured and compared using the Langmuir isotherm, which characterises gas-solid phase adsorption [10]. The link between a material's surface covering and concentration of inhibitors is described by the Langmuir isotherm and it is expressed as: [11]

$$\frac{I_{inh}}{\theta} = \frac{1}{K_{ads}} + I_{inh} \quad (4)$$

Plotting $log\frac{I_{inh}}{\theta}$ against $logI_{inh}$ gave a linear relationship as shown in Figure (1). The parameters of Langmuir isotherm are presented in Table (2). The (R^2) value of 0.9885

indicate strong adherence to Langmuir adsorption isotherm. The application of Langmuir isotherm to the adsorption of Eco-Friendly Polyester inhibitor on surface of mild steel indicated that there is no interaction between the adsorbate and adsorbent [12].

Table (2) Adsorption Parameters for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

Sample No.	**1**	**2**	**3**	**4**	**5**	**6**
Inhibitor Concentration (ppm)	-	100	200	400	500	1000
Inhibitor Concentration (Mx10⁻⁴)	-	0.25	0.50	1.00	1.25	1.50
Surface Coverage (θ)	-	0.6732	0.7279	0.8086	0.8285	0.9072
Inhibitor Concentration (Mx10⁻⁴)	-	67.32	72.79	80.86	82.85	90.72
(θ)/(1-θ)	-	2.05997	2.67512	4.22466	4.83098	9.77586
Adsorption Constant (K_{ads}) M^{-1}		8.23990	5.35024	4.22466	3.86478	3.91034
Adsorption Energy (ΔG°_{ads}) (kJ.mol⁻¹)	-	- 15.18	- 14.11	- 13.52	- 13.31	- 13.33

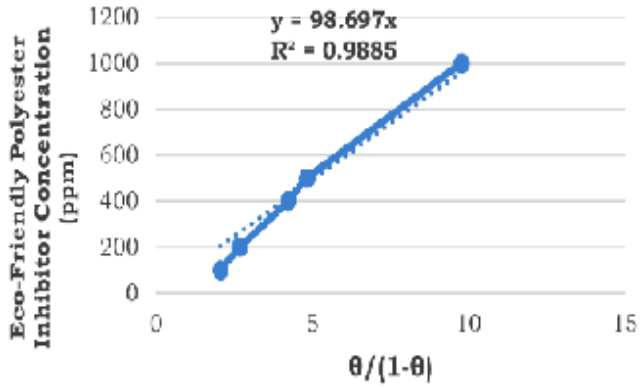

Figure (1) Langmuir Isotherm for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

4.3 Temkin Adsorption Isotherm

According to equation, the Temkin adsorption isotherm's coefficient of surface coverage (θ) and inhibitor concentration (I_{inh}) are connected [13, 14, 15]:

$$Exp\,(-2a\theta) = K_{ads}\, I_{inh} \tag{5}$$

Figure (2) shows plots of θ vs $logI_{inh}$. (R^2) has a value of 0.9964. Because (R^2) is greater than 0.9 and close to unity, it may be concluded that the experimental data fits the Temkin adsorption isotherm well [16, 17]. Set table caption with the number flush left above table. Horizontal lines should be placed above and below table headings and at the bottom of the table. Vertical grid lines should be avoided.

Table (3) Temkin Parameters for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

Sample No.	1	2	3	4	5	6
Surface Coverage (θ)	-	0.6732	0.7279	0.8086	0.8285	0.9072
Inhibitor Concentration Logarithm log (I_{inh}) (ppm)	-	2.0000	2.2010	2.6021	2.6990	3.0000

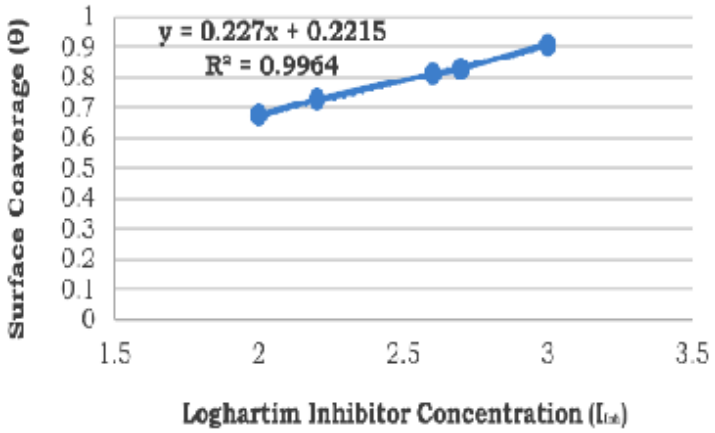

Figure (2) Temkin Isotherm for Adsorption of Eco-Friendly Polyester inhibitor on the Mild Steel Surface.

4.4 Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm model has been selected as the third option for assessing the absornant solution's adsorption potential. The equation yields the Freundlich isotherm [18]:

$$log(\theta) + \log(K_{ads}) + nlog(I_{inh}) \quad (6)$$

Where, n is the interaction parameter. The parameters of Freundlich isotherm are shown in Table (4). Figure (3) displays a plot of $log\theta$ vs. $logI_{inh}$ that shows a linear relationship and a (R^2) value of 0.9961, indicating that the isotherm that results from the adsorption of an Eco-friendly polyester inhibitor on a mild steel surface is obeying the Freundlich isotherm model. A plot of $log\theta$ vs. $logI_{inh}$ is shown in Figure (3), which gives a linear relation with (R^2) value 0.9629, which indicated that the adsorption of Eco-Friendly Polyester inhibitor on the mild steel surface, the isotherm is obeying to Freundlich isotherm model.

Table (4) Freundlich Parameters for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

Sample No.	1	2	3	4	5	6
Logarithm Surface Coverage (log (θ)	-	- 0.1719	- 0.1379	- 0.0923	- 0.0817	- 0.0422
Inhibitor Concentration Logarithm log (Iinh) (ppm)	-	2.0000	2.2010	2.6021	2.6990	3.0000

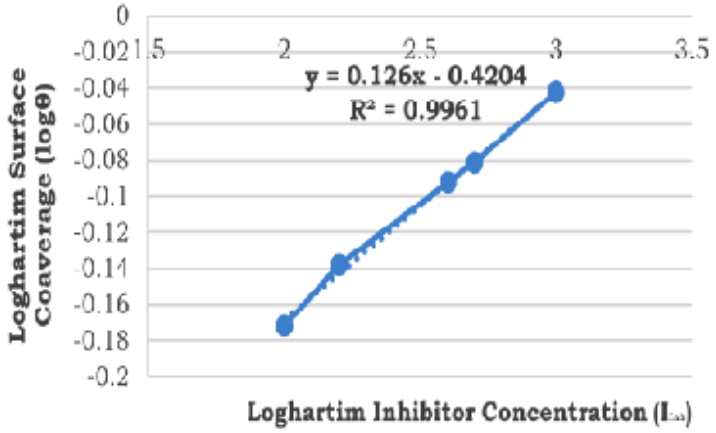

Figure (3) Freundlich Isotherm for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

4.5 Adejo Ekwenchi Adsorption Isotherm

Prior to reaching the maximum value of surface cover, the Adejo Ekwenchi isotherm establishes an inverse relationship between the amount of adsorbate uptake from the bulk concentration and the difference between the total available surface on the adsorbent surface and the fraction that is covered by the adsorbate at that temperature [19]. It is given by the equation:

$$log\left(\frac{1}{1}_{\theta}\right) + \log(K_{ads}) + blog(I_{inh}) \quad (7)$$

Where, *b* parameter is used to determine the mode of adsorption of an inhibitor on the metal surface. Table (5) displays the Adejo Ekwenchi isotherm's parameters. Figure (4) shows a plot of *log(1/1- θ)* vs. *logIinh* reveals a linear relationship with a (R^2) value of 0.9759, demonstrating that the isotherm for the adsorption of Eco-Friendly Polyester inhibitor on the surface of mild steel obeys the Adejo Ekwenchi isotherm model. The parameters of Adejo Ekwenchi isotherm are shown in Table (5).

Table (5) Adejo Ekwenchi Parameters for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

Sample No.	1	2	3	4	5	6
(1/1- θ)	-	3.0600	3.6751	5.2247	5.8309	10.7757
log(1/1- θ)	-	0.4587	0.5653	0.7181	0.7657	1.0324

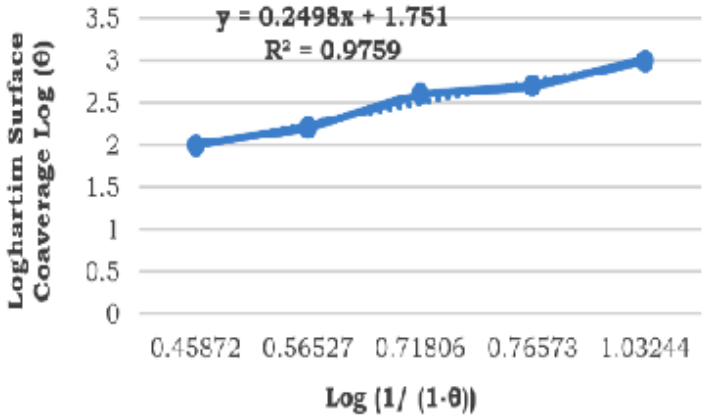

Figure (4) Adejo Ekwenchi Isotherm for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

4.6 El-Awady Adsorption Isotherm

The El-Awady isotherm model was fitted to the experimental data. The equation represents the model's characteristic [20]:

$$log\left(\frac{\theta}{1-\theta}\right) + \log(K_{ads}) + y log(I_{inh}) \quad (8)$$

Where, y represents the number of active sites.
The values of *log(θ /1- θ)* required for El-Awady isotherm are shown in Table (6). Figure (6) shows a plot of *log(θ /1- θ)* vs. $logI_{inh}$ reveals a linear relationship with a (R^2) value of 0.9659, demonstrating that the isotherm for the adsorption of Eco-Friendly Polyester inhibitor on mild steel surfaces follows the El-Awady isotherm model.

Table (6) El-Awady Parameters for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

Sample No.	1	2	3	4	5	6
log(θ /1- θ)	-	0.3139	0.4173	0.6258	0.6840	0.9902

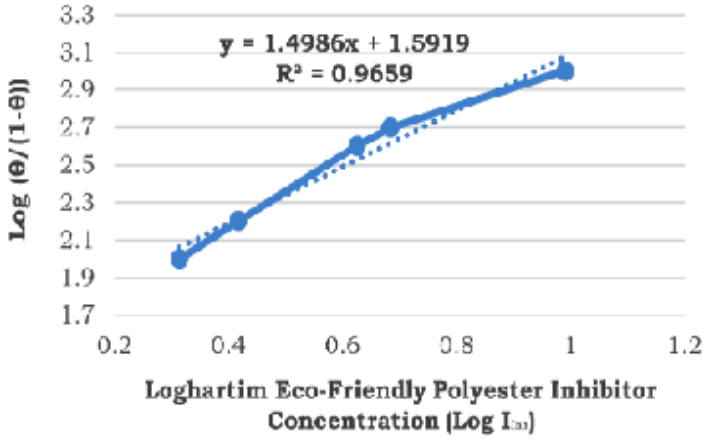

Figure (6) El-Awady Isotherm for Adsorption of Eco-Friendly Polyester Inhibitor on the Mild Steel Surface.

5. Conclusions

Five adsorption isotherms models were used to investigate the adsorption behaviour of Eco - Friendly Polyester inhibitor on the surface of mild steel material. Based on the obtained results of the adsorption isotherm plots, the adsorption of Eco-Friendly Polyester inhibitors on carbon steel from aqueous avid medium obey to whole of the used isotherm models including Langmuir, Temkin, Freundlich, Adejo Ekwenchi, and El-Awady, the obtained correlation factors (R^2) for these models were 0.9885, 0.9964, 0.9961, 0.9759 and 0.9659 respectively. The Temkin isotherm model amongst the others gave the best fit since having the highest regression (R^2) value. Eco-Friendly Polyester inhibitor has been identified as it has a very excellent adsorption on the surface of mild steel. The mechanism of adsorption proposed for the Eco-Friendly Polyester inhibitor is physiosorption since the values of ($\Delta G°_{ads}$) are ranged in between (-15.18 to -13.31 $kJ.mol^{-1}$) and the negative and high values of ($\Delta G°_{ads}$) indicated that there is a strong and spontaneous adsorption of inhibitor on the mild steel metal surface. Thus, it can be concluded that Eco-Friendly Polyester inhibitor system was found to be in good agreement with the experimental results as a corrosion inhibitor to protect a surface of mild steel which has been approved by (Seham Shahen, 2019), and as it has a very excellent adsorption on the surface of mild steel metal as approved in the present paper research.

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